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54 Cast detergent-containing article and method of making and using.

57 Solid cast detergent-containing articles are produced for use in automatic washing machines. A liquid detergent composition is cast onto a mold where it is allowed to solidify. The solid cast detergent, surrounded on all but its upper surface by the mold, is used in automatic washing machines. The cast detergent composition includes an alkaline hydratable chemical and optionally further includes one or more preformed cores or plugs comprising an available chlorine source, a defoamer, or the like.

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CAST DETERGENT-CONTAINING ARTICLE
AND METHOD OF MAKING AND USING

The drawings and the references to the drawings are
deemed to be deleted (Rule 43 EPC).

RECEIVING SECTION

13 MARS 1979

Field of the Invention

This invention relates a novel solid cast detergent-containing article which is particularly useful in institutional dishwashing machines and industrial washing machines. Another aspect of this invention relates to a method for producing the detergent-containing article. Another aspect of this invention relates to a method for using the detergent-containing article. Still another aspect of this invention relates to a method for isolating reactive and incompatible components within a solid cast detergent to minimize interaction between them during manufacture, storage, and dispensing.

Description of the Prior Art

Conventional institutional and industrial spray washing machines employ liquid or powdered detergents which are generally added to the wash tank by means of an automatic dispenser system. All forms of such detergents, whether liquid or solid, have stability problems and other problems associated with their manufacture, dispensing, and use. These problems have been discussed extensively in prior art publications and patent literature, and it is not practical to do anything more than summarize these discussions. In the early days of the development of solid detergents, when these detergent products were relatively low in performance compared to the products of today, the problems were less severe. However, the advent of high performance products, stimulated in part by increased esthetic and sanitary standards and a demand for shorter wash times has generally been characterized by the development of more complex detergent compositions which are more hazardous to the user, less stable, and more difficult to dissolve in a satisfactorily uniform manner.

For example, higher performance solid detergents generally means higher alkalinity (e.g. greater concentrations of sodium hydroxide) - higher even to the point of posing safety hazards to the user. Historically, detergents used for warewashing have been relatively low in alkalinity. The extensive use of aluminum trays and

utensils, the presence of soft metals in wash pump impellers and other factors generally prevented the use of high alkalinity detergents. Recently, however, there has been a trend toward the use of high alkalinity, higher performance products. This trend has been partially the result of the increased usage of stainless steel and corrosion resistant plastics in the production of utensils. In addition, the aforementioned increased standards and shorter wash times (usually ten seconds or less) required by the increased volume of business in eating establishments have created a demand for these higher performance products.

In addition to alkali metal hydroxides (e.g. sodium hydroxide), chemicals used in high performance products, particularly for hard surface cleaning (e.g. warewashing) include phosphates, silicates, chlorine containing-compounds, defoamers and organic polyelectrolyte polymers. See U.S. Patent No. 3,166,513, issued Jan. 19, 1965 (Mizuno, et al), U.S. Patent No. 3,535,285, issued Oct. 20, 1970 (Sabatelli, et al), U.S. Patent No. 3,579,455, issued May 18, 1971 (Sabatelli, et al), U.S. Patent No. 3,700,599, issued Oct. 24, 1972 (Mizuno et al) and U.S. Patent No. 3,899,436, issued Aug. 12, 1975 (Copeland, et al). The alkali metal hydroxides in these compositions are very effective in removing most stubborn food soils, but a source of available chlorine is usually included to control food stains, such as tea and coffee stains. The defoamer is usually included to control foam created by a proteinaceous soil and saponified fats. The use of chlorinated cyanurates as a source of available chlorine in detergents used to clean hard surfaces is disclosed in U.S. Patent No. 3,166,513, issued Jan. 19, 1965 (Mizuno, et al), U.S. Patent No. 3,933,670, issued Jan. 20, 1976 (Brill, et al), U.S. Patent No. 3,936,386, issued Feb. 3, 1976 (Corliss, et al). These patents also describe various means for obtaining storage stable chlorine bearing detergents. The use of defoamers in detergent compositions is disclosed by U.S. Patent No. 3,048,548, issued Aug. 7, 1962 (Martin, et al), U.S.

Patent No. 3,334,147, issued Aug. 1, 1967 (Brunelle, et al), and U.S. Patent No. 3,442,242, issued May 13, 1969 (Rue, et al).

One problem associated with detergents containing both
5 an active chlorine source and an organic defoamer has
been a substantial loss of available chlorine in a
relatively short period of time. This problem is described
in a number of the above references and in the article
10 by R. Fuchs, J. Polkowski, and Carfagno, "Agglomerated
Automatic Dishwasher Detergents," Chemical Times and
Trends, Pages 37-42 (Oct. 1977). One solution to this
problem has been to absorb the organic defoamer onto an
inorganic carrier particle, thus "encapsulating" the
15 defoamer, see U.S. Patent No. 3,306,858, issued Feb. 28,
1967 (Oberle). While a chlorine stability problem is
present in low alkalinity detergents containing defoamers,
the problem is more acute with high alkalinity detergents
because many defoamers and chlorine-containing compounds
20 are not stable in the presence of highly alkaline chemicals
such as sodium hydroxide.

In addition to the chlorine stability problem, several
additional problems have existed with high performance
powdered detergent compositions which have been used in
institutional and industrial washing machines. One of
25 these problems has been caused by differential solubility
of the detergent components. Not all of the components
of standard detergents dissolve at the same rate or have
the same equilibrium solubilities. For example, a fine,
soluble particle such as sodium dichloroisocyanurate
30 dihydrate, a common source of available chlorine, will
dissolve much more rapidly than sodium tripolyphosphate,
a common detergent component. Thus, when a dispenser is
charged with a powdered detergent containing both of
these components, the first effluent from the dispenser
35 will usually be over-rich in available chlorine while
the last effluent before the dispenser is recharged
will usually be poor in available chlorine.

Another type of differential solubility problem exists
with many common defoamers. Many defoamers have an oily

consistency and sparingly water soluble. When detergents containing these defoamers are dispensed from a conventional water-in-reservoir dispenser, the oily defoamer floats to the top and feeds the wash tank in an erratic fashion.

Another problem may exist with a powdered detergent if its components are of different particle sizes and densities. Variations in particle size and density between components may lead to segregation during manufacturing, shipping, and handling. Even when uniform distribution can be achieved during manufacturing, handling and shipping may cause segregation. Segregation leads to non-uniformity in the composition of the detergent when it is withdrawn from the container. Agglomeration of the components has been used to minimize the segregation problem. However, the use of agglomeration usually requires recycling of any particles which are too large or too small, which can be a significant percentage of the product.

Returning again to the safety hazard problem, one commonly used approach involves dispensing powdered or liquid detergents directly from their shipping container.

In any event, it is desirable for safety and convenience to minimize contact between the user and the high-performance detergent composition, and such lessened contact can be one of the many benefits of automatic dispensing. In the case of liquid detergents, it is relatively easy to provide an automatic dispensing system and method. For example, liquid detergents can simply be pumped into the wash tank or reservoir directly from their shipping containers.

Solid detergents (which can be in briquette, or, most typically, in powdered form) present much more complicated automatic dispensing problems. Several approaches have been devised for attacking these problems - that is, for utilizing solid phase detergents without losing the benefits of automatic dispensing. In one approach, detergents used in large conveyor type machines are dispensed directly from their shipping

containers by means of a dispensing system similar to that described in U.S. Patent No. 3,595,438, issued July 27, 1971 (Daley, et al). The shipping container is inverted and placed over a detergent dispenser reservoir and a water spray is used to dissolve the detergent from the drum as needed. A system for dissolving powdered detergent from a five to ten gallon capacity shipping pail is also known, see U.S. Patent No. 4,020,865, issued May 3, 1977 (Moffat, et al). In short, the solid powdered detergent in the shipping container is not in a form which normally would be introduced directly into the wash tank of the washing machine, it is generally preferred in the art to convert the powder into a liquid, e.g. by dissolving the powder with water in a special apparatus designed to carry out the dissolving step.

The dissolving apparatus need not be physically remote from the washing machine. Indeed, it is a common practice to mount dissolving/dispensing devices directly above - or on the side wall of - the wash tank of the machine. One typically used type of machine-mounted dispenser is the so-called water-in-reservoir type. (The water-in-reservoir approach is not limited to machine-mounted dispensers, however; in machine-mounted applications, the water-in-reservoir dispenser is generally used in a single tank warewashing machine.) Typically, the water-in-reservoir type of dispenser makes up a concentrated solution of detergent from the powder in the reservoir by means of swirling action or agitation provided by incoming water. The concentrated solution is delivered directly to the wash tank by gravity or through a delivery tube. The concentration of the detergent in the wash tank can be maintained at a preset level by means of a conductivity sensing controller similar to that described in U.S. Patent No. 3,680,070, issued July 25, 1972 (Nystuen).

Various other types of devices will dissolve and dispense powdered detergents and can be mounted directly on the washing machine. For example, U.S. Patent No. 4,063,663, issued Dec. 20, 1977 (Larson, et al) described

a type of dispenser in which the powdered detergent is placed over a conical or hemispherical screen and an aqueous spray from beneath the screen is used to dissolve the detergent. The concentrated solution produced by the spray is collected and directed to the wash tank. This dispenser differs from the water-in-reservoir type in that there is no water standing in the powder dispenser and the bulk of the powder remains dry. Otherwise, this type of dispenser operates in a manner similar to the water-in-reservoir type.

Among the other types of powdered detergent dispensers are small dispensers which hold from four to six pounds of detergent. The hopper of such dispensers can be filled from detergent-containing drums by means of a scoop or by the use of small individual (i.e. two pound) pouches of detergent. Dispensing systems for washing systems consisting of multiple hoppers which are filled with different chemicals or mixtures of chemicals are also known.

Dispensing systems for dispensing briquettes of detergent are also known in the art. See U.S. Patent No. 2,382,163, 2,382,164, 2,382,165 all issued August 14, 1945 to MacMahon and U.S. Patent No. 2,412,819, issued Dec. 17, 1946 (MacMahon). The detergent briquettes are dispensed from a modified water-in-reservoir round, pot-shaped dispenser. The briquettes (usually three) are held in a mesh basket which forms a slot about 1 1/4 inches wide across the diameter of the pot. The dissolving action is provided by a stream of water directed against the lower-most briquette and from the swirling action of water around the submerged portion of the lower-most briquette. Like the water-in-dispenser type devices, water is left standing in the reservoir. This type of system has the advantage of making it visually possible to determine when the detergent dispenser reservoir needs replenishing.

The MacMahon patents also disclose detergent briquette compositions and methods of manufacturing the briquettes. The briquette compositions and the methods

of manufacture which are disclosed appear to require the presence of a silicate and trisodium polyphosphate or sodium carbonate. Detergent bars or cakes comprising a significant level of an organic detergent and tripolyphosphates are also known. See U.S. Patent No. 3,639,286, issued Feb. 1, 1972 (Ballestra, et al). Compressed tablets containing detergents are also known, see U.S. Patent No. 2,738,323, issued Mar. 14, 1956 (Tepas, Jr.) and U.S. Patent No. 3,417,024, issued Dec. 7, 1968 (Goldwasser).

In the field of dispensing solid detergent to conventional institutional and industrial washing machines for spray cleaning of hard surfaces (e.g. warewashing), the briquette detergent approach does not appear to have attained the same degree of commercial success as powdered detergents.

Summary of the Invention

It has now been found that the chlorine stability, differential solubility, segregation, and safety problems described above can be minimized by forming a solid cast detergent in a disposable mold and dispensing or using the detergent directly from the mold/cast detergent combination. That is, the combination of the cast detergent and the disposable mold in which it was formed provides an article of commerce capable of dispensing dissolved solids from substantially only one surface - the surface which was the free or unsupported surface casting in the mold. This detergent article can be designed or structured to further minimize chlorine stability and differential solubility problems, e.g. by including the chlorine source and/or the defoamer as preformed plugs or cores encased in the cast detergent composition.

Thus, the present invention involves a process for forming and a method for using a three-dimensional, solid cast detergent composition containing an alkaline hydratable solid component, at least one other solid component, and a receptacle-shaped mold surrounding and containing the detergent composition on all but one surface. The detergent

composition is normally formed by mixing and heating the components in an aqueous solution, allowing the solution to cool and thicken as hydration of the hydratable component or components occur, pouring the solution into a mold and allowing the mixture to solidify. The aforementioned preformed plugs or cores of additional components can be inserted in the mixture after it has been added to a mold and before it has solidified.

The cast detergent composition is left in the disposable mold in which it was cast and is used by placing the mold in a detergent dispensing apparatus where the detergent is dissolved from the mold through the open portion of the mold by the use of a liquid spray.

Brief Description of the Drawings

FIGURE 1 is a partial cut-away side view of a disposable mold containing the cast detergent of this invention.

FIGURE 2 is a cross-sectional view of a disposable mold containing the cast detergent of this invention.

The cast detergent includes a preformed plug or core comprised of an additional ingredient or ingredients.

FIGURE 3 is a top view of the article illustrated in FIGURE 2.

FIGURE 4 illustrates the article of FIGURES 2 and 3 placed in an apparatus for dispensing the detergent composition.

FIGURE 5 is a graph comparing the chlorine recovery for a cast detergent prepared according to this invention versus a conventional powdered detergent.

Detailed Description

Raw Materials

One necessary component for producing cast detergent compositions of the present invention is a hydratable chemical. The term "hydratable chemical" as used herein includes chemicals forming both discrete and continuous states of hydration and thus means a chemical which is capable of absorbing or combining with water (e.g. 0.2-20 moles of water per mole of chemical) to form either type or state of hydration. The hydratable chemical will

normally be alkaline, that is, a one weight-percent aqueous solution of the chemical will have a pH of greater than 7.0 at 23° C. Since the detergent compositions used in this invention are highly alkaline, it is preferred that the hydratable component of the composition be alkaline in nature. Hydratable chemicals useful in the practice of this invention include alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide; silicates, such as sodium metasilicate; phosphates, particularly phosphates of the formula $MO \{PO_3M\}_n$ or the corresponding cyclic compounds $PO_3M \{PO_3M\}_n PO_3M$, wherein M is an alkali metal and n is a number ranging from 1 to about 60, typical examples of such phosphates being sodium or potassium orthophosphate and alkaline condensed phosphates such as sodium or potassium pyrophosphate, sodium tripolyphosphate, etc.; carbonates, such as sodium or potassium carbonate; borates, such as sodium borate; zeolites, etc. Combinations of two hydratable chemicals, for example, sodium hydroxide and sodium tripolyphosphate, have been found to work particularly well in the practice of this invention.

A second necessary component of the detergent composition of this invention is water. Water is used to form a solution containing the detergent components; the solution being cast into a mold and solidifying as the hydratable chemical or chemicals form a hydrate with the water. Water may be added as a separate ingredient or in combination with one of the other components, for example as an aqueous solution of 50% sodium hydroxide.

To obtain the advantages of this invention, at least two solid components are needed. If only one solid component were used, differential solubility and segregation problems would not exist and there would be few advantages to forming a cast composition. The advantages of a cast detergent composition over a conventional powdered detergent composition are described more fully hereinafter.

In addition to those components previously described, other conventional detergent components and fillers can be

included. For example, it is common to include a source of available chlorine and a defoamer. Many chlorine sources can be used including chlorinated isocyanurates, such as sodium dichloroisocyanurate dihydrate, and

5 hypochlorites, such as sodium and lithium hypochlorite. As more fully hereinafter described, when an available chlorine containing component is included in the composition of this invention it is preferably incorporated in the composition as a preformed plug or core. Defoamers are

10 also normally included in detergent compositions. Typically, a "defoamer" is a chemical compound with a hydrophobe/hydrophile balance suitable to reducing the stability of foam. The hydrophobicity can be provided by an oleophilic portion of the molecule (e.g. an aromatic

15 alkyl or aralkyl group; an oxypropylene unit or oxypropylene chain, or other oxyalkylene functional groups other than oxyethylene, e.g. tetramethylene oxide). The hydrophilicity can be provided with oxyethylene units or chains or blocks and/or ester groups (e.g. organo-phosphate

20 esters), salt-type groups, or salt-forming groups. Typically, defoamers are nonionic organic surface-active polymers having hydrophobic groups or blocks or chains and hydrophilic ester-groups, blocks, units, or chains, but anionic, cationic, and amphoteric defoamers are known.

25 For a disclosure of nonionic defoaming surfactants, see U.S. Patent No. 3,048,548, issued Aug. 7, 1962 (Martin, et al), U.S. Patent No. 3,334,147, issued Aug. 1, 1967 (Brunelle, et al), and U.S. Patent No. 3,442,242, issued May 13, 1969 (Rue, et al). Phosphate esters are also

30 suitable, e.g. esters of the formula $RO (PO_3M)_n R$, wherein n is as defined previously and R is an organic group or M (as defined previously), at least one R being an organic group such as an oxyalkylene chain. If a defoamer is included it may be included as a preformed plug or core,

35 as more fully described hereinafter. If it is included as a preformed core or plug it must be a solid, or be capable of being combined with other components to form a solid, at room temperature. Wax-like materials can be used to further isolate the chlorine source or defoamer in the

core from the surrounding cast article.

The Detergent Composition

The hydratable chemical or combination of hydratable chemicals will normally comprise at least 30%, and preferably 60%, by weight of the cast detergent composition. The water of hydration will normally comprise at least 15%, and preferably 25%, of the cast detergent composition. Performance improving additives such as available chlorine producing components and defoamers will normally comprise minor amounts of the composition, that is, less than 5%.

Typical three-component compositions of this invention can be formulated from (1) a phosphate or other hardness-precipitating or hardness sequestering agent, (2) an alkali metal hydroxide, and (3) water. Typical four or five component compositions would further include a defoamer and/or a neutral inorganic salt (alkali metal halides, sulfates, etc.) and/or a chlorine source and/or a thickening agent, thixotrope, suspending agent, or the like.

Typical detergent compositions of this invention employ a condensed alkali metal phosphate for the sequestering of hardness (Mg^{++} and Ca^{++} ions). However, alternatives to the condensed phosphates are known; see, for example U.S. Patent No. 3,535,285, issued Oct. 20, 1970 (Sabatelli, et al), U.S. Patent No. 3,579,455, issued May 18, 1971 (Sabatelli, et al) U.S. Patent No. 3,700,599, issued Oct. 24, 1972 (Mizuno, et al), and U.S. Patent No. 3,899,436, issued Aug. 12, 1975 (Copeland, et al).

One embodiment of the solid, cast detergent-containing article of this invention is generally shown by number 1 in FIGURES 1 through 3. The article includes disposable container or mold 3 into which base detergent 2 was cast or allowed to solidify. During shipping, article 1 will normally include lid or cover 5. Lid or cover 5 can be made of the same or similar material as used to make mold 3. As will be explained subsequently, this material is ordinarily alkaline-resistant, non-breakable, and inexpensive. Expensive corrosion-

resistant metals or plastics can be used, if provision can be made for their recycling, but "disposable" materials would normally be preferred for most institutional uses.

As illustrated in FIGURE 2, the cast detergent composition is surrounded by and in contact with mold 3 on all but the upper surface of the solid cast detergent.

In a preferred embodiment of this invention, cast detergent base 2 will include one or more preformed plugs or cores 6, as illustrated in FIGURES 2 and 3. At least one preformed plug will normally comprise a chlorine source. When a plurality of preformed plugs are used they will normally comprise different, incompatible ingredients. For example, one plug could comprise a chlorine source while a separate plug could comprise a defoamer. By incorporating a chlorine source in one preformed plug and a defoamer in a separate preformed plug, degradation of the chlorine source, and the resultant loss of available chlorine, which often occurs when chlorine sources and defoamers come in contact, can be minimized. Thus, by incorporating preformed plugs of incompatible ingredients in the solid, cast detergent composition of this invention, the stability problems associated with many conventional powdered detergents can be minimized. To minimize reactivity between the base detergent and any material added as preformed cores, the core material may be optionally encased in a film or material which would not react with the core material or the detergent base. This coating could be comprised of a natural wax, a synthetic wax, a phosphate ester, or the like.

Some active chlorine sources such as calcium hypochlorite have been found to react very slowly at the plug-base detergent interface and would not normally need to be encased in a film or the like. However, other chlorine sources such as sodium dichloroisocyanurate dihydrate have been found to be more reactive, in which case a protective film would be beneficial.

Mold or container 3 can be made of any alkali-resistant material which can withstand moderately elevated

temperatures, e.g. 150° F., and which can be formed into and hold the desired shape. Since the mold is generally intended to be "disposable" (i.e. not intended for re-use as a mold), inexpensive materials are preferred such as thermoplastics, resin-impregnated heavy paper or cardboard, and the like. Inexpensive but fragile materials such as glass or ceramics are less preferred due to handling or shipping problems, relatively flexible materials being preferred. Molds made of plastic (e.g. inexpensive thermoplastics) have been found to be particularly useful.

Method of Manufacturing

While the following process is described with reference to specific components, it should be understood that other components and similar processes can be used to form a detergent solution which can be cast into a mold and will solidify upon hydration of its hydratable component. A particularly useful detergent composition of this invention is formed by heating about 50-75 parts by weight of a 50-75 weight percent aqueous solution of an alkali metal hydroxide, e.g. sodium hydroxide, to about 55° to 65° C. While other alkali metal hydroxides may be used, sodium hydroxide has been found to be particularly useful and the following method of manufacturing will be described with respect to it. Aqueous solutions of 50 weight percent sodium hydroxide are readily commercially available. Solutions containing higher weight percents of sodium hydroxide are also available (e.g. 73%) or can be produced by adding a desired amount of anhydrous sodium hydroxide to a 50 weight percent solution of sodium hydroxide. An aqueous solution of sodium hydroxide can also be prepared by mixing water and anhydrous sodium hydroxide in the desired ratio.

After the aqueous solution of sodium hydroxide reaches a temperature of about 55° to 65° C., 30 to 40 parts by weight of anhydrous sodium tripolyphosphate are added to the solution. Since the sodium tripolyphosphate will not normally completely dissolve, it is kept suspended by continuous mixing. After the sodium tripolyphosphate has

been added other optional fillers and components may be added if desired. The solution is then allowed to cool with continuous mixing. After approximately ten to fifteen minutes the mixture will begin to thicken. As it begins to thicken, the mixture is poured into a receptacle-shaped mold to a level at least part way up the side molding surfaces. As the mixture continues to cool it will solidify to form a cast composition. While solidification is due partially to cooling, it is believed that it is mainly due to the hydration of the sodium tripolyphosphate or products derived therefrom and to a lesser degree, the sodium hydroxide. After it has solidified, the cast detergent is surrounded by and in contact with the mold on all sides except for its upper surface which remains exposed.

After the base detergent has been poured into the mold, but before it has solidified, preformed cores or plugs such as plug 6 in FIGURES 2 and 3 may be added. When a plug is added, the base detergent is allowed to solidify around it and retain it in place. While any shape or size plug could be used, it is normally preferred that the plug extend to the entire depth of the base detergent as illustrated in FIGURE 2. The plug should extend the depth of the solidified detergent so that a constant ratio of components can be maintained while the base detergent and the plug are dissolved during use.

An alternative method of including a separately formed plug or plugs could consist of using a mold comprising one or more smaller molds positioned within the larger mold. The large mold would be filled with the cast detergent base while the smaller mold or molds would contain separate compositions such as a source of available chlorine or a defoamer. The compositions could be cast into the smaller mold or preformed as a plug and "pressed" into the mold.

35 Method of Use

The solid, cast detergent-containing article of this invention is normally used as illustrated in FIGURE 4. FIGURE 4 illustrates detergent dispensing apparatus 10 which can be part of a conventional institutional or

industrial washing machine (not shown). Article 1, including base detergent 2, preformed core 6, and container 3 is placed in an inverted position over spray means 12 which is connected to a water source 14. When water source 14 is turned on, spray means 12 causes water to impinge on the exposed surface of detergent 2 and core 6. The detergent and the core dissolve and flow through pipe 13 to the wash tank of the washing machine (not shown). Detergent base 2 and preformed core 6 can be formulated to dissolve at substantially the same rate and thus supply the tank with a consistent ratio of ingredients.

By controlling the spray time the amount of detergent, and thereby the concentration of detergent, in the wash can be controlled.

The present invention will be further understood by reference to the following specific examples which are illustrative of the composition, form and method of producing the solid, cast detergent-containing article of this invention. It is to be understood that many variations of composition, form and method of producing the cast detergent would be apparent to those skilled in the art. The following examples, wherein parts and percentages are by weight unless otherwise indicated, are only illustrative.

Example 1

An 8.8 pound batch (approximately 4000 grams) of a solid cast detergent of this invention was prepared using the following procedure.

Fifty-five parts by weight of a 50 weight percent aqueous solution of sodium hydroxide were added to a laboratory mixer provided with a stirring means and a heating means. The 50% sodium hydroxide solution was heated to approximately 55°-60° C. Nine parts by weight of anhydrous sodium hydroxide were added to the solution. The solution was stirred until the anhydrous sodium hydroxide had the effect of forming an approximately 57 weight percent aqueous solution of sodium hydroxide.

Thirty-six parts of anhydrous sodium tripolyphosphate were added to the solution and the solution was mixed.

The tripolyphosphate did not completely dissolve but was held in suspension by mixing. Mixing was continued without heating until the solution began to thicken, which was approximately 10-15 minutes after the addition of the tripolyphosphate.

After the mixture had thickened but while it was still pourable, six pounds (about 2700 grams) were poured into a receptacle-shaped mold such as mold 3 in FIGURES 1-3, consisting of a slightly tapered cylindrical plastic container measuring about 6 1/2 inches (about 16.5 cm) at the major diameter (the open end) and about 5 1/2 inches (about 14 cm) at the minor diameter and about 4 1/2 inches (about 11.5 cm) in depth. The mixture was allowed to harden in the mold which took approximately 5 minutes.

The composition of the final cast product (in weight-%) was approximately:

36.5% sodium hydroxide

27.5% water

36.0% sodium tripolyphosphate

100.0%

While this product can be used as a detergent without additional additives, additional components can be included as illustrated in the following examples.

Example 2

A product with the same composition as that described in Example 1, with the exception that 1 part by weight of the 50% sodium hydroxide was replaced with 1 part by weight of a defoamer, was produced. The defoamer was added following the addition of the sodium tripolyphosphate and was kept uniformly dispersed by continuous mixing until the mixture was poured in the mold. At the time it was poured the mixture was sufficiently viscous so that a uniform dispersion was maintained.

The composition of the final cast product (in weight-%) was approximately:

- 18. -

36% sodium hydroxide
27% water
36% sodium tripolyphosphate
1% defoamer
100%

5

Example 3

A mixture was prepared according to the procedure described in Example 1. 53.57 parts of 50% sodium hydroxide, 8.77 parts of anhydrous sodium hydroxide, and 35.06 parts of anhydrous sodium tripolyphosphate were used. The mixture was then poured into the mold described in Example 1. Before the mixture completely solidified 2.6 parts of a preformed circular "plug" measuring about 1 inch in diameter (about 2.5 cm) and about 3 1/2 inches (about 9 cm) in length, comprising a source of available chlorine, was placed approximately in the center of the mold. The length of the plug was such that it extended from the bottom of the mold to the surface of the mixture. The mixture was then allowed to harden around the plug.

20 The composition of the solidified cast detergent (in weight-% was:

35.5% sodium hydroxide
26.8% water
36.1% sodium tripolyphosphate
2.6% chlorine plug
100.0%

25

The available chlorine containing plug was prepared by forming a composition consisting of:

59.7 parts calcium hypochlorite - 65% available
chlorine (HTHtm from Olin-Mathieson)
14.4 parts Veegum® WG (from R.T. Vanderbilt
Company, Inc.)
25.9 parts dendritic sodium chloride
100.0

30

35 "Veegum" is a trademark for inorganic suspending agents.

After the three ingredients were mixed, plugs measuring about 1 inch (about 2.5 cm) in diameter and about 3 1/2 inches (about 9 cm) in length, were made by

filling an appropriate size cylindrical die with the composition and subjecting the die to about 2,000 psi in a hydraulic press.

Plugs containing available chlorine were produced following the same procedure from the two following compositions:

A. 100 parts Lithium Hypochlorite 35% available chlorine

B. 51.4 parts sodium dichloroisocyanurate dihydrate
14.4 parts Veegum® WG
34.2 parts dendritic sodium chloride
100.0 parts total

Plugs produced from these formulas were also found to perform satisfactorily in the article of this invention

Example 4

This example was designed to illustrate how plug 6 of FIGURES 2 and 3 could be further isolated from the base detergent. One plug was made from each of the following formulas by compression molding at about 2000 psi mold pressure.

41.0g (59.9%) calcium hypochlorite - 65% available chlorine
10.0g (14.3%) Veegum® WG
18.0g (25.8%) dendritic salt
69.9g (100%)
41.5g (59.7%) sodium dichloroisocyanurate dihydrate
10.0g (14.4%) Veegum® WG
18.0g (25.9%) dendritic salt
69.5g (100%)

Both plugs were dipped in melted paraffin wax which was held at just above its melting point of 56.5° C. so that a very thin coating of paraffin wax was formed on the sides and one end of the plug. The wax was allowed to cool and harden. The plugs were then inserted into the cast detergent base of Example 2 following the procedure of Example 3. No visual indication of any reaction at the plug-detergent base interface was noted with either of

these plugs.

Example 5

A mixture was prepared following the procedure described in Example 2. 52.57 parts of 50% sodium hydroxide, 8.77 parts of anhydrous sodium hydroxide, 35.06 parts of anhydrous sodium tripolyphosphate and 1 part defoamer were used. The mixture was then poured into the mold described in Example 1. Before the mixture completely solidified, 2.6 parts of a chlorine containing plug similar to those described in Example 3 was added as described in Example 3.

The composition of the solidified cast detergent was:

35.0% sodium hydroxide

26.3% water

35.1% sodium tripolyphosphate

1.0% defoamer

2.6% chlorine plug

100.0%

Example 6

A solid cast detergent of the same formula as that described in Example 5 was produced. However, instead of mixing the defoamer with the base detergent it was added in the form of a plug. Thus, two plugs were used, one comprising a defoamer and the other comprising a source of available chlorine. The two plugs were placed near the center of the mold after the detergent was added, but before it solidified.

The composition of the solidified cast detergent was:

35.0% sodium hydroxide

26.3% water

35.1% sodium tripolyphosphate

1.0% defoamer plug

2.6% chlorine plug

100.0%

The defoamer plug was prepared by heating together 60 parts of a viscous (at room temperature) polyoxyalkylene glycol and 40 parts of a solid mixture of mono- and di-alkyl

phosphate esters until the phosphate esters melted and then mixing until the mixture was uniform. The solution was then poured into a cylindrical mold and allowed to cool and form a solid plug at room temperature.

- 5 Similar plugs were produced following essentially the same procedure using: 50 parts of a polyethylene glycol, 25 parts of a polyoxyalkylene glycol, and 25 parts of a mixture of mono- and di-alkyl phosphate esters.

Example 7

- 10 A solid cast detergent was produced using the same formula and procedure as described in Example 2 except that the 1 part of defoamer was added as a plug similar to those described in Example 6.

Example 8

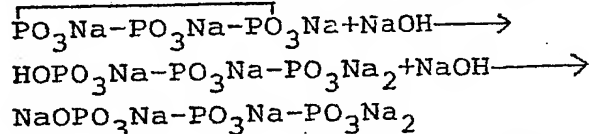
- 15 Approximately 6 pounds of a solid cast detergent of this invention were prepared using the following procedure. 40 parts of anhydrous sodium metasilicate and 39 parts of a 10 weight percent aqueous solution of sodium hypochlorite were added to a laboratory mixer provided with a stirring
20 means and a heating means. The solution was heated to approximately 55°-60° C. Twenty parts of anhydrous sodium tripolyphosphate were added to the solution and the solution mixed without heating until it began to thicken. After the mixture had thickened but while it was
25 still pourable it was poured into a mold consisting of the dimensions described in Example 1. Before the mixture completely solidified, 1 part of a defoamer plug similar to those described in Example 6 was added following the previously described procedure.

- 30 The composition of the solidified cast detergent was approximately:

- | | |
|----|-----------------------------|
| | 40% sodium metasilicate |
| | 35% water |
| | 20% sodium tripolyphosphate |
| 35 | 4% sodium hypochlorite |
| | <u>1% defoamer plug</u> |
| | 100% |

Example 9

This example was designed to illustrate that the sodium tripolyphosphate component of the previous examples can be formed in-situ by reacting sodium trimetaphosphate with sodium hydroxide via the following reaction:



Approximately 2200 ml of 50% aqueous sodium hydroxide was added to a stainless steel, jacketed beaker equipped with a Lightning stirrer. Following the addition the temperature was 70° F. (21° C.). Next 1440 g of powdered trimetaphosphate was added slowly. As the temperature of the mixture approached 100° F. (38° F.), cooling was applied. The remainder of the trimetaphosphate was added incrementally until the entire 1440 grams had been added. During the addition a maximum temperature of 200° F. (93° C.) was reached.

Upon sitting for several minutes the mixture formed a solid which could have been cast into a mold and used as the solid, cast detergent of this invention.

Example 9A

This example illustrates that chlorinated trisodium phosphate may be used as the chlorine source. A solid cast detergent having the following composition was prepared:

25	36.0% caustic soda
	27.0% water
	36.0% sodium tripolyphosphate
	<u>1.0% defoamer</u>
30	100.0%

The above mixture was prepared using the procedure as described for Example 2. The mixture was poured (about 2360 g) into the mold which had a removable 2 inch diameter cylinder placed in the center. After the mixture had solidified, the 2 inch diameter cylinder was removed leaving a hollow cylindrical cavity. This hollow cavity was filled with about 340 grams of molten chlorinated trisodium phosphate. The chlorinated trisodium phosphate solidified upon cooling below its melting point. Some

reaction occurred at the interface of the plug. It is believed that this reaction may be reduced significantly allowing the cast detergent to cool thoroughly before the chlorinated trisodium phosphate was poured and/or coating the cavity surface with an inert barrier such as, for example, paraffin wax or mixed mono and dialkyl esters of polyphosphoric acid or like materials.

Example 10

This example was designed to illustrate the production of a non-phosphate solid, cast detergent. Forty parts of 50% aqueous sodium hydroxide was heated to 150° F. (65.5° C.) in a jacketed stainless steel beaker equipped with a stirrer. Twenty parts of anhydrous sodium hydroxide were added and the mixture was stirred until a molten solution was formed. Twenty-five parts of liquid silicate (RU silicate from Philadelphia Quartz) having an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 2.54 was added and resulted in the temperature of the mixture increasing to about 200° F. (93° C.). The mixture was cooled to about 150° F. (71° C.) and 15 parts of sodium polyacrylate were added slowly while stirring continued.

The mixture was poured into a plastic container where it solidified upon cooling.

Example 11

The purpose of this example is to compare the consistency of available chlorine recovery from a cast detergent-containing article produced according to the instant invention and a conventional, prior art, powdered detergent. The prior art formula used consisted of a mixture of sodium tripolyphosphate, sodium dichloroisocyanurate (a chlorine source), sodium metasilicate, and sodium hydroxide. Sodium dichloroisocyanurate comprised approximately 28% of the formula. The cast detergent-containing article used was produced by the process and using the formula described in Example 5. The chlorine source was present in the form of a plug situated approximately in the center of the cast base detergent. The cast detergent containing article was dispensed from an apparatus similar to the one illustrated

in FIGURE 4. The prior art formula was dispensed from a water-in-reservoir dispenser of the type illustrated in Figure 1 of U.S. Patent No. 3,680,070, issued July 25, 1972 (Nystuen).

5 Samples of the effluent from the dispensers were collected periodically and titrated for alkalinity to the phenolphthalein end point with hydrochloric acid and titrated for available chlorine with sodium thiosulfate using the conventional iodometric titration. The influent
10 water temperature to both dispensers was about 71° C. (160° F.).

 The amount of detergent present in the effluent was determined by the alkalinity of the effluent. The "chlorine recovered-percent of theoretical" (CRPT) was then calculated
15 from the formula:

$$\text{CRPT} = \frac{\text{available chlorine in effluent}}{\text{available chlorine expected in effluent (from detergent present)}} \times 100$$

 The results are illustrated in Figure 5. Figure 5 shows
20 that the solid cast detergent of this invention provides very uniform chlorine recovery when compared to a prior art formulation. It is theorized that the differential solubility of the components of the prior art powdered detergent is responsible for the more erratic chlorine
25 recovery shown by the prior art detergent.

Example 12

 This example was designed to determine the effect of segregation during the manufacture of conventional, prior art powdered detergent. Since there should be no segregation with the solid cast detergent of this invention;
30 (since all the components are physically locked in place) any significant segregation with a powdered detergent would represent a disadvantage of the powdered detergent.

 The conventional powdered detergent used was the same
35 as that described in Example 11. This powdered detergent is commonly packaged in two-pound packages. Seven two-pound packages from the same production batch were selected at random for analysis. Ideally each of the packages should contain the same percentage of each of the four ingredients.

The contents of each of the packages were weighed and the entire contents dissolved in an appropriate quantity of water in a 30 gallon drum to give a 1% weight/volume solution. This eliminated any variation due to the possibility of different amounts of detergent being present in different packages. A 100 ml sample was withdrawn from each drum and titrated for available chlorine with sodium thiosulfate using the standard iodometric titration. The results were as follows:

	<u>Sample No.</u>	<u>Percent Available Chlorine</u>
10	1	1.63
	2	2.00
	3	1.53
	4	1.56
15	5	1.54
	6	1.96
	7	1.65

As indicated, the percentage of available chlorine varied from 1.53 to 2.00. This variation is in part due to segregation during mixing and packaging of the powdered detergent. This segregation is probably one factor leading to the variation in chlorine delivery illustrated in Figure 5.

Example 13

This example was designed to compare the chlorine stability of cast detergents of this invention containing a chlorine source directly in the base detergent with cast detergents of this invention which incorporate a chlorine source as a core or plug, such as those described in Example 3. Three different chlorine sources were used: sodium dichloroisocyanurate dihydrate ($\text{NaDCC} \cdot 2\text{H}_2\text{O}$), lithium hypochlorite (LiOCl), and calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). All of the compositions were produced following the procedure of Example 1 with the chlorine source being added directly to the mixture following the addition of the sodium tripolyphosphate in one case and the chlorine being added as a plug in the other. In the third case the chlorine source plug was dipped in a paraffin was (m.p. 52.5°) and in a fourth case the chlorine

source plug was dipped in mono and dialkyl ester of polyphosphoric acid, a wax-like solid (m.p. 150-160° F.). The formula used and the available chlorine remaining after various storage times at room temperature are shown in Table I.

As indicated by Table I, when the chlorine source is added directly as a component of the cast detergent most of the chlorine is lost within 24 hours. However, when the chlorine source is added directly as a component of the cast detergent most of the chlorine is lost within 24 hours. However, when the chlorine source is incorporated into the cast detergent as a preformed core or plug, excellent chlorine stability results with $\text{Ca}(\text{OCl})_2$ and lithium hypochlorite but not with $\text{NaDCC} \cdot 2\text{H}_2\text{O}$. When the chlorine source plug was coated with a film of paraffin wax or a waxy mono and dialkyl ester of poly phosphoric acid the best stabilities were obtained.

TABLE 1
CHLORINE STABILITY

Components*	CHLORINE SOURCE ADDED DIRECTLY TO DETERGENT			CHLORINE SOURCE ADDED AS PLUG			CHLORINE SOURCE ADDED AS PLUG BUT COATED WITH PARAFFIN			CHLORINE SOURCE ADDED AS PLUG BUT COATED WITH PE-053		
	Ca (OCl) ₂	LiOCl	NaDCC-2H ₂ O	Ca (OCl) ₂	LiOCl	NaDCC-2H ₂ O	CaOCl	LiOCl	NaDCC-2H ₂ O	CaOCl	LiOCl	NaDCC-2H ₂ O
NaOH - 50%	52.4	51.0	52.2	52.57	52.57	52.57	52.57	52.57	52.57	52.57	52.57	52.57
NaOH Anhyd	9.0	9.0	9.0	8.77	8.77	8.77	8.77	8.77	8.77	8.77	8.77	8.77
STP	36.0	36.0	36.0	35.06	35.06	35.06	35.06	35.06	35.06	35.06	35.06	35.06
Defoamer	1.0	1.0	1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ca (OCl) ₂	1.6			2.60			2.60			2.60		
NaDCC-2H ₂ O			1.8			2.60			2.60			2.60
Li (OCl) - 35%		3.0			3.33			3.33			3.33	
Percent Available Chlorine remaining after 24 hours	3.5	17.4	3.5									
Percent Available Chlorine remaining after 29 days												
Percent Available Chlorine remaining after 15 days												
Percent Available Chlorine remaining after 2 days												
							60	1.5	100	99	100	100

*Components shown in parts by weight. These products essentially same as Product of Example 5.

Example 14

The purpose of this example was to compare the uniformity of delivery of defoamer from: (A) a conventional powdered detergent (Scoretm, a commercial product of Economics Laboratory, Inc.); (B) a cast detergent (product of Example 5); and (C) a cast detergent incorporating the defoamer as a core or plug (product of Example 6). All three of the formulations contained 1% by weight of defoamer. The (A) conventional detergent and (B) the product of Example 5 contained the same defoamer; (C) the product of Example 6 contained the blend of two defoamers described in Example 6 (the blend was used to obtain a solid product which could be molded into a plug).

All tests were conducted in a Hobart C-44 (trademark) single tank dishwashing machine. A C-11 Dispenser (trademark of Economics Laboratory, Inc.), a water-in-reservoir type dispenser, was used to dispense product (A) (the conventional powdered detergent). The Hobart C-44 (trademark) machine was equipped with a dispenser similar to that illustrated in Figure 4 for dispensing the solid cast detergent products (B) (product of Example 5) and (C) (product of Example 6). Both dispensers were controlled by a conductivity base controller of the type described in U.S. Patent No. 3,680,070, issued July 25, 1972 (Nystuen). The controller was set to maintain a 0.2% concentration of detergent in the wash tank. The water temperature was about 140° F. (65° C.) for all of the tests.

Defoamers are included in detergents for spray-wash machines to control foam created by food soils. Foam in a wash tank leads to entrapment of air in the wash solution being recirculated through the machine and results in a reduction in mass and kinetic energy and which leads to poor soil removal. Excess foam in a wash tank causes a loss in water pressure which can be measured by a manometer connected to the wash manifold up stream from the water pump. Egg is a common foam-causing food soil and was selected for use in this test.

The C-11 Dispenser optimally holds about four pounds of powdered detergent and thus four pounds of conventional detergent (A) were used in the test. Products (B) and (C) were approximately six pounds each and were of the configuration described in Example 1 and illustrated in Figures 1-4.

The pressure (in inches of water) was recorded when the dispenser was freshly charged, when about one-half of the detergent had been dispensed, and when about four-fifths of the detergent had been dispensed. Manometer readings were taken on the freshly charged detergent: (1) with water alone, (2) after the detergent was added, (3) five minutes after 115 grams of egg were added, and (4) five minutes after an additional 100 grams of egg were added.

Between the "Freshly Charged" test and the "Detergent 1/2 Spent" test, the fill valve was opened to deliver 2 gallons of water per minute for dilution to simulate normal dilution of the wash tank by rinse water which is diverted to the wash tank to freshen the wash water. The conductivity controller dispensed detergent as required to maintain a 0.2% concentration of detergent in the wash tank. When about one-half of the detergent originally in the dispensers was left, manometer readings were taken and the two egg additions described above repeated with readings being taken five minutes after each addition. The same procedure was repeated after about one-fifth of the detergent originally present was left in the dispensers (four-fifths spent).

The "Detergent 1/2 Spent" test was somewhat more severe than the "Freshly Charged" test and, likewise, the "Detergent 4/5 Spent" test was somewhat more severe than the "Detergent 1/2 Spent" test, due to the cumulative concentration of egg soil resulting because the wash tank was not drained between tests.

The results of these tests are summarized in Table II.

TABLE II

(A) Conventional Powdered Detergent	FRESHLY CHARGED		DETERGENT 1/2 SPENT		DETERGENT 4/5 SPENT	
	Wash Pressure (inches of water)	% Loss	Wash Pressure (inches of water)	% Loss	Wash Pressure (inches of water)	% Loss
Water alone:	43	--	--	--	--	--
Detergent added:	43	--	42.5	--	41.0	5.0
5 minutes after 115g. egg added:	38	12	26.0	40	25.0	42
5 minutes after additional 100g. egg added:	28	35	22.0	48	*	--
(B) Defoamer in Cast Detergent (Product of Example 5)						
Water alone:	42	--	--	--	--	--
Detergent added:	42	--	43	--	42.5	--
5 minutes after 115g. egg added:	42	0	43	0	41.0	3.0
5 minutes after additional 100g. egg added:	42	0	30	30	29.0	32
(C) Defoamer as Plug in Cast Detergent (Product of Example 6)						
Water alone:	42.5	--	--	--	--	--
Detergent added:	42.5	--	42	--	42.5	--
5 minutes after 115g. egg added:	42.5	0	42	0	41.0	0
5 minutes after additional 100g. egg added:	42.5	0	42	0	41.0	3.5

*Test was stopped due to excessive foam to avoid damage to pump and motor.

5 The data in Table II indicates that Product (C) (the product of Example 6 with the defoamer included as a plug) had the highest and most consistent wash pressures and that Product (B) (the product of Example 5 with the defoamer included in the cast detergent) had higher and more consistent wash pressures than Product (A) (the conventional powdered detergent). The higher and more consistent wash pressures indicate more uniform defoamer delivery.

10 It was noted that the defoamer incorporated in the powdered detergent (A) floated to the top and formed an oily film in the water-in-reservoir dispenser. It is believed that this resulted in slug-feeding of the defoamer instead of uniform delivery. In contrast, with the solid cast detergent of this invention, both the detergent and
15 defoamer are dispensed simultaneously which helps assure uniform dispensing of the defoamer.

WE CLAIM:

- 1 -

1. A detergent-containing article of commerce comprising:

5 a. a three-dimensional, solid cast detergent composition comprising at least two solid components; at least one of said solid components comprising an alkaline hydratable chemical; and

b. a receptacle-shaped mold surrounding and in contact with said solid cast detergent composition on all but one surface thereof.

10 2. The article of claim 1 wherein said mold is the mold in which said composition was cast and solidified.

3. The article of claim 2 wherein said hydratable chemical comprises at least 30% of said composition.

15 4. The article of claim 2 wherein said article further comprises a cover attached to the said receptacle-shaped mold.

20 5. The article of claim 2 wherein said article further comprises at least one preformed core, said core being surrounded by and in contact with said detergent composition on at least one side of said core.

6. The article of claim 5 wherein said preformed core comprises a source of available chlorine.

7. The article of claim 5 wherein said preformed core comprises a defoamer.

25 8. The article of claim 5 wherein said article comprises at least two preformed cores, at least one of said cores comprising a source of available chlorine and at least one of said other at least two cores comprising a defoamer.

30 9. The article of claim 5 wherein the said preformed core is separated from the said detergent composition by an inert barrier film.

10. A method for using the detergent composition of the detergent-containing article of claim 1 comprising:

35 a. placing said detergent-containing article in a detergent dispensing device for dispensing detergent into the article-washing zone of an article washing apparatus, whereby only the said side of the solid cast detergent composition not surrounded by

said receptacle-shaped mold is exposed to the interior of said detergent dispensing device, thereby providing said detergent dispensing device with essentially one unsurrounded, exposed surface of detergent composition;

b. impinging a flow of aqueous liquid upon said unsurrounded, exposed surface to form an aqueous liquid detergent containing said detergent composition in the aqueous liquid; and

c. dispensing said aqueous liquid detergent into said article-washing zone for the purpose of washing articles therein.

11. A process for forming a three-dimensional, solid cast detergent within a receptacle-shaped mold having side molding surfaces, said process comprising the following steps:

a. heating about 50-75 parts by weight of a 50-75 weight percent aqueous solution of an alkali metal hydroxide to about 55° to 65° C.;

b. distributing about 30 to 40 parts by weight of an alkaline hydratable chemical in said solution;

c. allowing said solution to begin to cool and thicken, and mixing said solution during said cooling and thickening;

d. pouring said thickened solution into said receptacle-shaped mold and filling said mold to a level at least part way up said side molding surfaces, the upper surface of the thus-poured, thickened solution being unsupported by said receptacle-shaped mold; and

e. allowing said solution to solidify in said mold, whereby a solidified surface of the solidified cast detergent is the said upper surface unsupported by said mold.

12. The process of claim 11 wherein said alkali metal hydroxide is sodium hydroxide.

13. The process of claim 12 wherein said alkaline hydratable chemical is added as sodium tripolyphosphate.

14. The process of claim 11 further comprising, following step (d) and prior to step (e), the step of inserting in said thickened solution in said mold at least one preformed plug composition.

5 15. The process of claim 14 wherein at least one of said at least one plug composition comprises a source of available chlorine.

16. The process of claim 14 wherein at least one of said at least one plug composition comprises a defoamer.

10 17. The process of claim 11 wherein the said hydratable material is selected from the group consisting of sodium or potassium phosphate.

18. The process of claim 11 wherein the said hydratable material is added as sodium polyphosphate.

15 19. The process of claim 11 wherein the said hydratable material added is selected from the group consisting of sodium or potassium trimetaphosphate.

20 20. The process of claim 11 wherein the product contains at least one polyelectrolyte water conditioning material.

21. A solid, cast detergent-containing article produced by the process of claim 11 comprising:

25 a. said solid cast detergent, and, surrounding and in contact with all but the said upper surface of said solid cast detergent,

 b. the said mold into which said solid cast detergent was cast, said mold acting as a container for said detergent.



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EUROPEAN SEARCH REPORT

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Application number

EP 79 10 0344

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	FR - A - 1 368 126 (SAVONNERIE ET MANUFACTURE DE PRODUITS CHIMIQUES DE PORT A L'ANGLAIS) * Abstract *	1	C 11 D 17/04 17/00 A 47 K 5/08
A	GB - A - 1 307 387 (RAION YUSHI KABUSHIKI KAISHA) * Claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 11 D 17/04 17/00 D 06 F 58/20 A 47 K 5/04 5/06 5/08
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
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